Self-interaction and molecular Coulomb blockade transport in *ab initio* Hartree-Fock theory

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We calculate the transport characteristics of a cobalt polypyridyl molecular complex in the Coulomb blockade regime using *ab initio* Hartree-Fock theory. We reproduce qualitative features of the Coulomb blockade such as integer charging and linear dependence of the maximum conductance bias with gate voltage, and we analyze the connections between such features and the correct description of electron self-interaction in a mean-field theory.

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I. INTRODUCTION

Experimental measurements on molecular devices are now sufficiently sensitive to explore many different electron transport phenomena, including Coulomb blockade transport and Kondo physics.[1–5] At the same time, theoretical descriptions of transport are now advancing to the stage where nonequilibrium I-V characteristics are obtainable through *ab initio* calculations.[6–14]

In this Brief Report, we examine transport characteristics of a molecular system in the Coulomb blockade regime, under conditions of variable gating and bias, within the *ab initio* Hartree-Fock mean-field approximation. We have used a cobalt polypyridyl complex of the type studied experimentally by Park *et al.*[2] The purpose of our calculations is not so much to provide data on the cobalt system *per se* but rather to illustrate how a qualitative picture of the Coulomb blockade in a realistic system emerges within the Hartree-Fock picture of conductance. While Coulomb blockade transport has been explored theoretically using many techniques including equation of motion theory,[15] slave-boson methods,[16] Fock-space rate equations,[17] and contour perturbation theories,[18] as recognized by earlier authors, many qualitative features of Coulomb blockade transport appear already at the mean-field level.[17,19,20] There it is linked to the description of electron self-interaction, and we examine this connection explicitly in this work.

II. COBALT POLYPYRIDYL COMPLEX

Our model molecule is the cobalt polypyridyl complex $(\mathrm{Co}[\mathrm{tpy}-(\mathrm{CH_2})_2-\mathrm{SH}]_2)^{n+}$ shown in Fig. 1. Molecules of this kind with varying lengths of the thiol linkers have been studied experimentally by Park *et al.*[2] The Coulomb blockade is associated with the transition from the low-spin Co^{3+} formal oxidation state to the low-spin Co^{2+} formal oxidation state. In our calculations, the cobalt complex is attached via thiol linkages to atomic chain gold electrodes.

We carried out transport calculations using our own prototype nonequilibrium Green's function (NEGF) code. Our implementation is similar to that of Brandbyge *et al.*[11] although we have used a finite cluster approximation to obtain the equilibrium part of the density matrix. As the NEGF equations have been given elsewhere many times, we refer the reader to the literature for details.[21,22] For the cobalt complex, we used an *ab initio* Hamiltonian in the STO-3G Gaussian basis.[23–26] The molecular geometry of the complex was optimized at the Hartree-Fock level; details are provided in the supplementary material. For the gold electrodes and the coupling matrix elements between the electrode and molecule basis functions, we used an extended Hückel Hamiltonian[27] and the equilibrium chemical potential was chosen to be −10.0 eV. An active space of 16 orbitals was derived for the molecule from a restricted Hartree-Fock calculation on the isolated (thiol-terminated) Co^{3+} complex. The orbitals were selected to be the 16 orbitals closest in energy to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), excluding the sulfur nonbonding orbitals. (The sulfur nonbonding orbitals would be perturbed strongly on attachment to the gold electrodes to form bonding and antibonding orbitals that would lie outside our chosen active-space energy window.) The resulting active-space orbitals were primarily π orbitals on the pyridyl ligands (Fig. 2). Both the restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) calculations for the complete molecule-electrode system were performed using the same active-space representation for the molecule. In the transport calculations, the bias voltage V was applied symmetrically as a chemical potential on the two electrodes $(\pm V/2)$, while the gate voltage was applied as a chemical potential g on the molecular active-space orbitals.

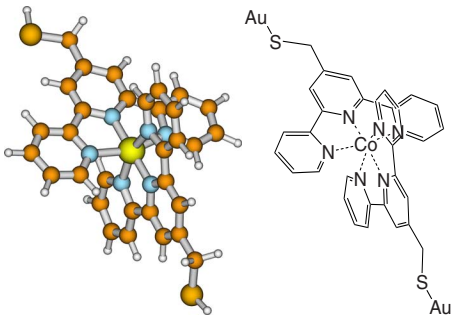

FIG. 1. (Color online) Cobalt polypyridyl complex. The Au (gold) terminating atoms in the left figure denote the beginning of the Au (gold) atomic chain electrodes.

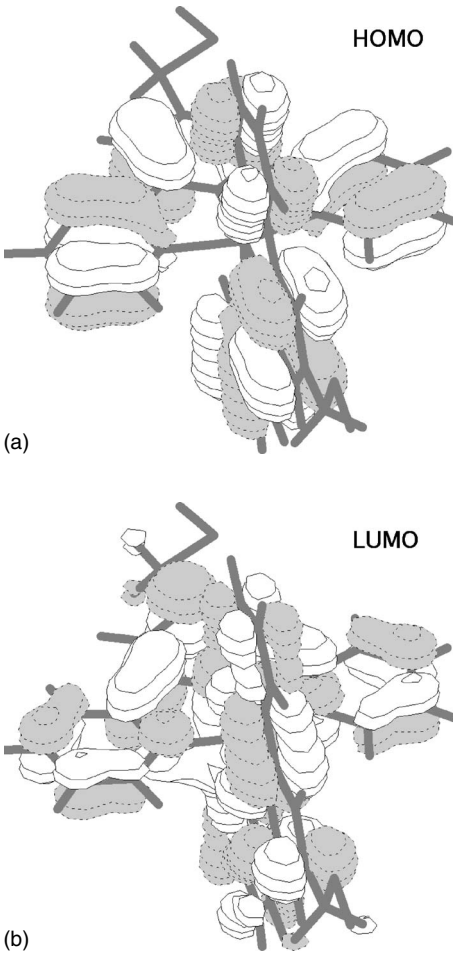

FIG. 2. Cobalt complex molecular orbitals.

III. CONDUCTANCE AND PARTICLE NUMBER AS A FUNCTION OF GATE AND BIAS

The results of our Hartree-Fock NEGF transport calculations for the cobalt polypyridyl complex are shown in Figs. 3–5. Figure 3 gives the current vs bias (I-V) curves at selected gate voltages. Figure 4 plots the oxidation state of the cobalt complex as a function of gate voltage at zero bias. (The oxidation state is evaluated from the occupation numbers of the orbitals which are primarily located on the complex; these are well localized because of the weak coupling to the electrodes.) Figure 5 gives the diamond plot of the differential conductance $\partial I/\partial V$ as a function of gate voltage g and bias V.

From these results, we observe the following qualitative features: (1) as the gate voltage (absolute value) increases, the molecule displays discrete integer charging (Fig. 4), (2) the maximum of the differential conductance peak shows a linear bias versus gate dependence (Figs. 3 and 5), (3) the linear dependence is interrupted by a discontinuity (Fig. 5), and (4) the maximum conductance in the Co^{2+} state is lower than that in the Co^{3+} state (Fig. 3). Compared with the experimental differential conductance plots by Park *et al.*,[2] our theoretical plot is qualitatively similar, although the overall conductance maximum is smaller. Features (1) and (2) and possibly (4) appear to be in qualitative agreement with experiment, while (3) appears to be an artifact of the theoretical approximation.

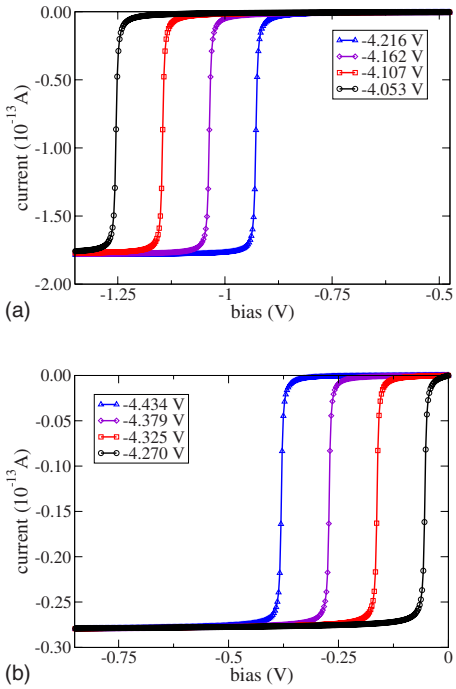

FIG. 3. (Color online) I-V curves at selected gate voltages.

Previous analysis of Coulomb blockade at the mean-field level (see, e.g., Refs. 17 and 20) has emphasized the appearance of spin-symmetry breaking in mean-field theory, and this explains many features of the Hartree-Fock conductance results. In the Co^{3+} system, the Hartree-Fock solution is restricted in nature, whereas in the Co^{2+} system, it is unrestricted, i.e., spin-symmetry breaking. The artifactual discontinuity in Fig. 5 arises because maximum conductance occurs when the LUMO or HOMO orbital eigenvalues are aligned with the biased levels of the electrode; i.e., $\mu \pm V/2$, where μ is the chemical potential of the electrodes. The gate discontinuity is, therefore, the orbital energy difference $\epsilon^{\mathrm{RHF}}_{\mathrm{LUMO}}(\mathrm{Co}^{3+}) - \epsilon^{\mathrm{UHF}}_{\mathrm{HOMO}}(\mathrm{Co}^{2+})$. Similarly, the decreased conductance in the Co^{2+} state within the Hartree-Fock calculations is due to spin-symmetry breaking, as the unrestricted solution permits transport only through one of the two spin channels.

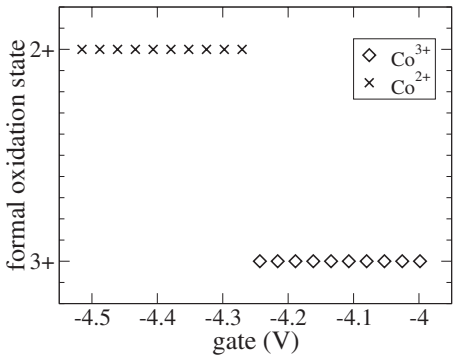

FIG. 4. Formal oxidation state of the cobalt complex as a function of gate voltage.

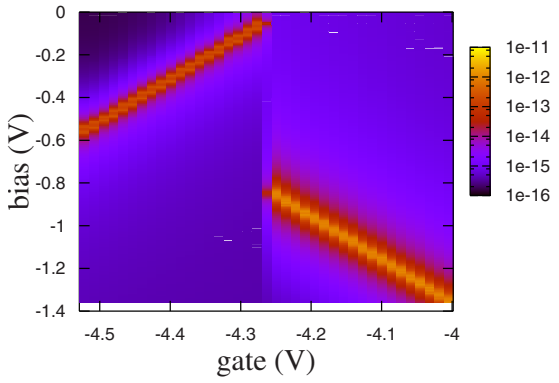

FIG. 5. (Color online) "Diamond" plot showing conductance (S) as a function of bias and gate voltages. (Brighter indicates larger conductance.) The discontinuity is an unphysical result arising from the mean-field spin-symmetry breaking: see text for discussion. (The largest conductance is observed only for a very narrow range of values near the center of the bright bands.)

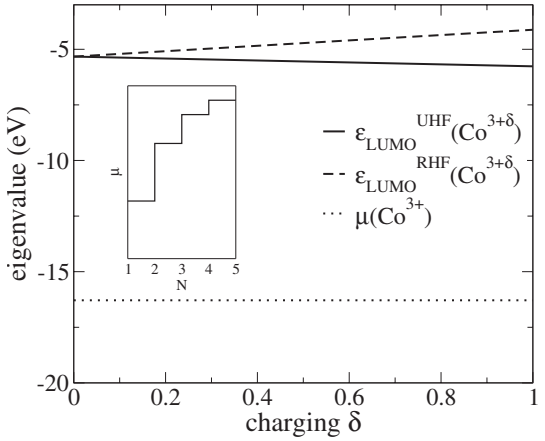

FIG. 6. LUMO eigenvalue as a function of charging δ. As δ increases, the UHF LUMO eigenvalue decreases monotonically, while the RHF LUMO eigenvalue increases monotonically. The monotonic decrease of the UHF LUMO eigenvalue is what allows for the reproduction of integer charging in the Hartree-Fock theory of Coulomb blockade. Inset: exact behavior of the chemical potential μ as a function of the number of electrons.

While the presence of qualitatively different restricted and unrestricted mean-field solutions on either side of a critical gate voltage permits a mean-field theory to emulate discrete jumps in particle number and conductance associated with Coulomb blockade charging, it does not fully explain the correct reproduction of features (1) and (2) in our results. For example, the molecule is formally an open system and the average particle number is a continuous variable. Thus, while spin-symmetry breaking should produce a jump in particle number, it need not produce the correct *integer* jump as observed. Similarly, it is not clear that a mean-field theory, where the eigenvalues have a nonlinear dependence on density and charging, should produce a simple linear relationship between the maximum conductance gate voltage and bias. As one may expect, both these features result from the particular mean-field approximation used, i.e., Hartree-Fock theory, and are related to the absence of self-interaction error. The role of self-interaction in quantum transport has previously been discussed by several groups.[19,28,29]

Let us first examine the discrete integer charging as a function of gate voltage, which is a hallmark of the Coulomb blockade. (We shall here assume zero bias and weak coupling.) In an exact theory, discrete integer charging in an open system characterized by a chemical potential $\mu = \partial E / \partial N$ occurs because μ exhibits discontinuities at integer values of N and consists of straight line segments in between.[19,30,31] Consequently, for gate potential g, the molecule possesses integer charge N such that $I < \mu(N) < A$, where I and A are the ionization energy and electron affinity of the molecule in the gate potential.

In a mean-field theory such as Hartree-Fock theory, the corresponding analysis requires examining the orbital eigenvalues as a function of charging in an open system. In a partially charged system such as the $Co^{3+\delta}$ complex, the LUMO orbital is partially occupied yielding an ensemble one-particle density matrix

$$\gamma(\mathrm{Co}^{3+\delta}) = \left(\sum_{i}^{\mathrm{HOMO}} |\phi_i\rangle\langle\phi_i| \right) + \delta |\phi_{\mathrm{LUMO}}\rangle\langle\phi_{\mathrm{LUMO}}|. \quad (1)$$

(Note that we have formally assigned the partial charge to the Co atom although, in practice, it is distributed also over the ligands.) The chemical potential of the $Co^{3+\delta}$ complex is given then by the LUMO eigenvalue; $\mu(\mathrm{Co}^{3+\delta}) = \epsilon_{\mathrm{LUMO}}(\mathrm{Co}^{3+\delta})$. The absence of partial charging implies that for any given μ, there are no lowest energy Hartree-Fock solutions with $\epsilon_{\mathrm{LUMO}}(\mathrm{Co}^{3+\delta}) \leqslant \mu$ for any value of δ other than 0 or 1. In Fig. 6, we have plotted the RHF and UHF LUMO eigenvalues $\epsilon_{\mathrm{LUMO}}(\mathrm{Co}^{3+\delta})$ of the isolated cobalt complex (using the active space defined in Sec. II) as a function of the partial charging δ. Partial charging was enforced by occupying the LUMO with δ electrons and building the density matrix using Eq. (1).

For unrestricted Hartree-Fock theory, we observe that $\epsilon_{\mathrm{LUMO}}(\mathrm{Co}^{3+\delta})$ decreases monotonically with δ. The *monotonic decrease* of the LUMO is the key to integer charging, as it ensures that as μ is raised from $\mu(\mathrm{Co}^{3+})$, the first allowed charging event is an integer charging, where $\mu = \epsilon^{\mathrm{UHF}}_{\mathrm{LUMO}}(\mathrm{Co}^{2+})$. [Subsequently, as μ is raised above $\epsilon^{\mathrm{UHF}}_{\mathrm{LUMO}}(\mathrm{Co}^{2+})$, we could, in principle, deplete the LUMO orbital until $\epsilon^{\mathrm{UHF}}_{\mathrm{LUMO}}(\mathrm{Co}^{2-\delta}) = \mu$; however this state would be higher in energy than the Hartree-Fock state with a completely filled LUMO, and it thus would not be the lowest energy ensemble consistent with μ.] In general, the behavior of the LUMO eigenvalue as a function of charging depends on the mean-field approximation employed. In the UHF theory, the primary effect of the additional δ charge in the LUMO is to increase the Coulomb potential felt by the electrons in the lower lying orbitals. Within the LUMO, however, the exchange interaction exactly cancels the electron self-interaction of the partial charge δ. In a frozen orbital

Hartree-Fock approximation, the LUMO eigenvalue would therefore be independent of δ. Relaxation of the orbitals has a tendency to lower the LUMO eigenvalue, and this gives rise to the monotonic decrease of ϵ_{LUMO} with δ. (In the restricted Hartree-Fock theory, both the α and β LUMO orbitals become partially filled and interact via the Coulomb interaction, thus giving rise to the increase of the LUMO eigenvalue with δ).

The exact cancellation of self-interaction in the LUMO is a feature of the unrestricted Hartree-Fock theory which does not generally occur in other unrestricted mean-field approximations, such as certain density functionals. These may therefore give rise to erroneous partial-charging in the Coulomb blockade regime as a function of gate voltage. An analogous partial charging occurs in the approximate density functional description of infinitely dissociated fragments,[30,31] and within transport calculations, is related to erroneous predictions of metallic transport in insulating molecules.[19]

The observed physical linear behavior of the maximum conductance bias as a function of gate within the Hartree-Fock approximation is closely linked to the faithful reproduction of integer charging. Although a nonlinear mean-field theory could, in principle, produce a nonlinear behavior of the eigenvalues with gate in the weakly coupled limit, this would require some form of charging which is here disallowed, except for integer charging. Thus, the effect of the constant gate voltage g is simply to shift the orbital eigenvalues by g, which immediately yields the linear relationship between g and the maximum conductance bias. When integer charging does occur, the subsequent discontinuity in the maximum conductance peak may be viewed in this context as an *extremely* nonlinear behavior of the eigenvalue arising from the mean-field nature of the theory.

To summarize, here, we have studied the transport characteristics of a cobalt polypyridyl complex in the Coulomb blockade regime using *ab initio* Hartree-Fock theory. We find that we can qualitatively reproduce the main features of the Coulomb blockade. While this is in part explained by the spin-symmetry breaking in the theory, we have shown that ultimately it is the correct description of electron self-interaction that is directly responsible for the reproduction of important Coulomb blockade features such as integer charging and linear dependence of maximum conductance bias on gate.

ACKNOWLEDGMENTS

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